Role of acetic acid on U(VI) sorption on silica

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The influence of acetate on U(VI) sorption on silica from aqueous solutions was studied at pH 2–7 by complementary experimental methods of macroscopic measurement, spectroscopic investigation and thermodynamic calculation. Sorption percentage of U(VI) in the absence and in the presence of different acetate concentrations was determined by batch sorption procedures. Attenuated total reflection Fourier transform infra-red spectroscopy (ATR-FTIR) was used to elucidate the mechanisms of uranyl sorption on silica in the presence of acetate, by investigating, *in-situ*, the changes in the U(VI) sorption on silica surface in presence of ligand: the absorption bands of carboxylate $\nu(COO)$ in the range 1300–$1700\,cm^{-1}$ and those around 850–$950\,cm^{-1}$ of uranyl species $\nu_{as}(UO_2)$ are followed. The decrease of U(VI) sorption with increasing acetate concentration was observed. Sorption of U(VI)-acetate (U-Ac) species on silica surface was demonstrated for the first time. ATR-FTIR investigations clearly evidenced the absorption bands characteristic of sorbed U-Ac complexes both from the acetate and uranyl spectral regions those the wavenumbers correspond to sorbed species. No sequence effect of acetate and uranyl on the sorption on silica in ternary systems U(VI)-acetate-silica was observed from the sorption data. From the ATR-FTIR investigations, we can induce that the sorption of U-Ac leads to chemical equilibria and makes possible the modeling of sorption isotherms by surface complexation models. The related thermodynamic constants were modeled using CCM surface complexation modeling.

Keywords: ATR, Uranyl, Sorption, Silica, Ternary systems

I. INTRODUCTION

In the context of long-term safety of radioactive waste repositories, our general focus is to follow the role of the short-chain carboxylic acids in the sorption of uranyl ions onto silica (chosen as model surfaces of clays). Low molecular weight organic acids, being cellulose degradation products, are ubiquitous in ground and surface waters and have functional groups encountered in the natural organic matter [1–3]. In this paper, the role of acetic acid in the sorption of U(VI) onto silica is investigated.

A detailed structural characterization of sorption is an indispensable step for understanding and modeling the surface reactions induced from aqueous solutions. Because of the probing of a thin sample layer whilst limiting the water absorbance contribution, attenuated total reflection Fourier-transform infra-red spectroscopy (ATR-FTIR) is used to follow the *in-situ* sorption of aqueous metallic ions or organic molecules onto mineral surfaces. This technique can be performed from metallic oxide suspensions after batch experiments or from formation of a deposit on an ATR crystal of high refractive index. The latter procedure was developed by different authors [4, 5] and used in the coating the ATR crystal by a layer of colloidal mineral particles dried under N_2. The layer was contacted to an aqueous solution containing the ions to sorb in order to follow the sorption as a function

of time and composition of the solution (pH, ionic strength, concentrations of ions or molecules to sorb, etc.).

In this paper, the *in situ* sorption procedure from coating the ATR crystal by a layer of colloidal mineral particles, developed by Hug [4] and applied by Lefèvre *et al.* [5–7] and Müller [8, 9] to the sorption of actinide ions on mineral surfaces, is used to investigate the sorption mechanisms of uranyl ions on silica in presence of acetate. This is done by following the sorption bands of carboxylate (in the range of 1300–$1700\,cm^{-1}$) and of uranyl species (850–$950\,cm^{-1}$). Influence of the acetate in the sorption of uranyl ions on silica, and effect of the addition order of acetate and uranyl in the ternary system silica-U-Ac, are reported and discussed.

II. METHODS AND MATERIALS

A. Chemical and solutions

All chemicals used were of analytical reagent grade. Acetic acid was provided by Sigma-Aldrich®. Sodium perchlorate hydrate (99.99%) ($NaClO_4 \cdot H_2O$) was provided by Sigma-Aldrich®. $UO_2(NO_3)_2 \cdot 6\,H_2O$ (> 99% FLUKA®purity) was used. Silica (SiO_2) (particle sizes of 0.2–$0.5\,mm$, specific area of $380\,m^2/g$) was supplied by Merck®. All solutions were prepared with deionised water (Millipore®direct Q, resistivity $= 18.2\,M\Omega$).

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B. Batch sorption experiments

The procedure used in this study was similar to that described in Ref. [10]. All sorption experiments were carried out at room temperature. Silica suspensions of $10\,\mathrm{g/L}$ were prepared in a $10\,\mathrm{mL}$ electrolyte solution ($NaClO_4$) adjusted to the desired pH and ionic strength. The tubes were mechanically shaken for 48 h for hydration of solids. U(VI) or organic stock solutions were added to the suspensions simultaneously by different orders as needed. pH values were adjusted by adding $HClO_4$ or NaOH. The solution was equilibrated for 24 h. This duration was determined by kinetics studies (sorption equilibrium vs. contact time), the results showed that the minimal kinetics for uranyl sorption equilibrium was 6 h; and the U(VI) sorption percentage remained constant in the following 2 days. Although no sorption was measured for acetate ion, we chose 24 h as the equilibrium time in both binary (uranyl/silica or acetate/silica) and ternary (uranyl/acetate/silica) sorption systems. The sorption samples were then centrifuged at a rate of 3000 rpm for 30 min to separate solid material from aqueous solution. The supernatants (filtered if needed) were used to measure the pH values and the sorption percentage of analytes by the silica gel. The sorption percentage (% *Sorbed*) was defined as

$$\%Sorbed = [(C_{\mathrm{ref}} - C_{\mathrm{surp}})/C_{\mathrm{ref}}] \times 100\%, \qquad (1)$$

where C_{ref} and C_{surp} represent the concentrations of analytes (mol/L) in reference solutions (prepared under the same experimental conditions of pH, ionic strength, and initial concentration of analytes as sorption sample, without silica) and in surpernatants. U(VI) and Organics concentrations were determined by TRLFS (Time Resolved Laser Fluorescence Spectroscopy) and TOC (Total Organic Carbon) analyzer, respectively.

C. ATR-FTIR experiments

The spectra were investigated by FT-IR using the ATR technique. The silica films were prepared directly on the surface of the ATR diamond crystal (Pike MIRacle®). The ATR accessory was a horizontal diamond crystal ($\varPhi 4\,\mathrm{mm}$) with an internal reflection on the upper surface in an incident angle of $45°$. An aliquot of $1\,\mathrm{\mu L}$ of silica aqueous suspension ($10\,\mathrm{g/L}$) was pipetted onto the crystal with subsequent drying under a gentle N_2 flow. This procedure was repeated ten times to have a homogeneous layer and in these conditions the sorption process was reproducible. The mineral layer deposited on the crystal was first rinsed with a background electrolyte solution of same properties (pH, temperature, ionic strength) as the containing uranyl or organic to sorb, by connection to a $50\,\mathrm{mL}$ vessel through a peristaltic pump at flow rate of $0.5\,\mathrm{mL/min}$, according to the procedure described in Ref. [5]. All measurements were performed under liquid nitrogen bubbling to prevent the uptake of carbon dioxide in the solution.

FT-IR spectra were measured in a dry air-purged compartment of a Thermo Scientific Nicolet 6700 spectrometer equipped with a mercury cadmium telluride (MCT) detector.

The spectral resolution was $4\,\mathrm{cm}^{-1}$ and the spectra were averaged over 256 scans. ATR-FTIR spectra were collected using the OMNIC®software for data processing. Spectra of sorbed species were decomposed by Gaussian functions using ORIGIN®software with the peak fitting module (PFM).

D. Surface complexation modeling

Surface complexation models can be used to describe the sorption of ions on charged surfaces by assuming that adsorption involves both a coordination reaction at specific surface sites and an electrostatic interaction [11]. Optimisation of model parameters was performed using the nonlinear least squares simulation code FITEQL 4.0 [12]. Constant capacitance model (CCM) was used to describe the sorption of U(VI) on oxides at high ionic strength ($\geq 0.1\,\mathrm{M}$) [13].
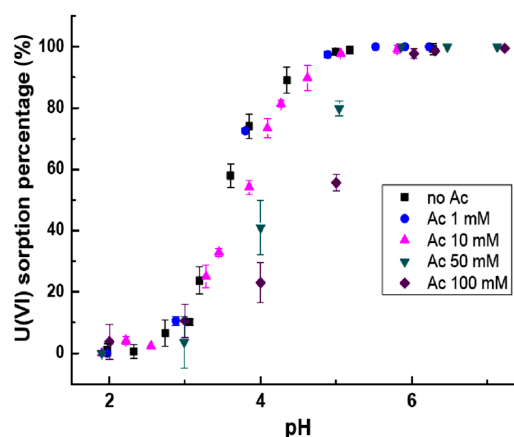

Fig. 1. (Color online) Percentage sorption of 0.1 M U(VI) on silica in absence and in presence of acetate (1, 10, 50 and 100 mM) at pH 5.4. $I = 0.1\,\mathrm{M}$.

III. RESULTS AND DISCUSSION

A. Effect of acetic acid

The effect of acetic acid on U(VI) sorption by silica was studied in the concentration range of 0–$100\,\mathrm{mM}$. Fig. 1 shows the sorption profiles of U(VI) as function of pH in presence of acetic acid at different concentrations. The results were obtained by macroscopic measurements of uranyl quantities in the supernanants issued from batch sorption experiments. In U(VI)/silica binary system, U(VI) sorption increased rapidly with pH of the supernatants and remained constant at 100% after pH 5. In the U(VI)/acetate/silica ternary systems, the presence of $[Ac] \leq 10\,\mathrm{mM}$ did not change much the sorption profile of U(VI) on silica. However, the presence of $[Ac] = 50\,\mathrm{mM}$ and $100\,\mathrm{mM}$ decreased effectively the sorption percentage of U(VI) and the sorption edge shifted to higher pH. This behaviour could be attributed to the formation of U(VI)-carboxylate soluble complexes (Fig. 2), which

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could establish a new chemical equilibrium in the solid-liquid interface. It should be pointed out that the surface complexation constants were optimized in the context of U(VI) aqueous speciation described by the thermodynamic data from NEA database [14] and Martell [15]. The speciation diagram of U(VI)-acetate in aqueous solution were realized using MEDUSA software.
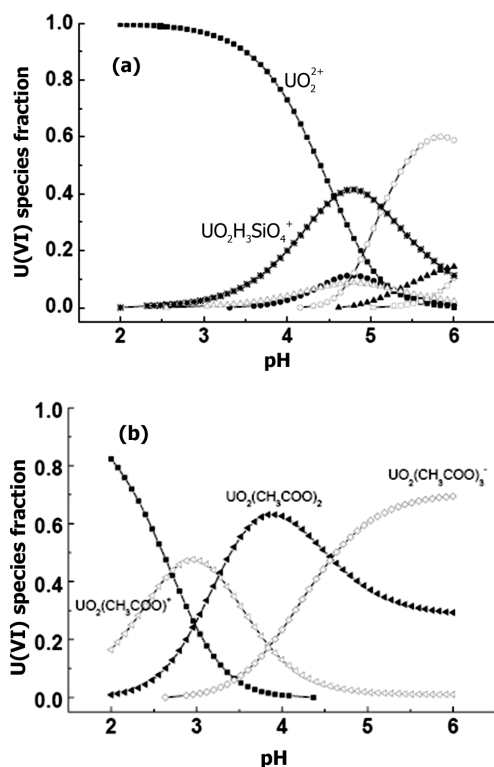

Fig. 2. Speciation diagrams of uranyl ions (0.1 mM) as a function of pH and in the absence (a) and the presence of acetate 100 mM (b). UO_2^{2+} (■), $UO_2H_3SiO_4^+$ (∗), UO_2OH^+ (△), $(UO_2)_2(OH)_2^{2+}$ (●), $(UO_2)_3(OH)_5^+$ (○), $(UO_2)_4(OH)_7^+$ (▲), $UO_2CO_3(OH)_3^-$ (□), $UO_2(CH_3COO)^+$ (◁), $UO_2(CH_3COO)_2$ (◀), $UO_2(CH_3COO)_3^-$ (◇).

In this pH range, the speciation of uranyl ions is mainly governed by U-Ac complexes: $(AcO)UO_2^+$, $(AcO)_2UO_2$ and $(AcO)_3UO_2^-$ with the relative proportions varying with pH and acetate concentration. This results in decreased sorption of U(VI) on silica surface, suggesting a competition between organic ligand and silica surface for U(VI) complexation. The similar decrease in the sorption of uranyl ion on silica was observed in the presence of citric acid [16]. From the sorption edge analysis, characterized by the increasing U(VI) sorption with pH, we favor a "metal-like" sorption type [17] in binary and ternary systems.

The effect of ionic strength ($NaClO_4$ of 0.01–2 M) on U(VI) sorption by silica in the absence (Fig. 3(a)) and presence (Fig. 3(b)) of 100 mM organic acids was investigated. The ionic strength had negligible effect on U(VI) sorption, suggesting an inner sphere surface complexation for U(VI) on silica [18]. Thus, we can choose a simple model for electrostatics (see Section III C), i.e. constant capacitance model, as the presence of a plane dedicated to outer-sphere complexed
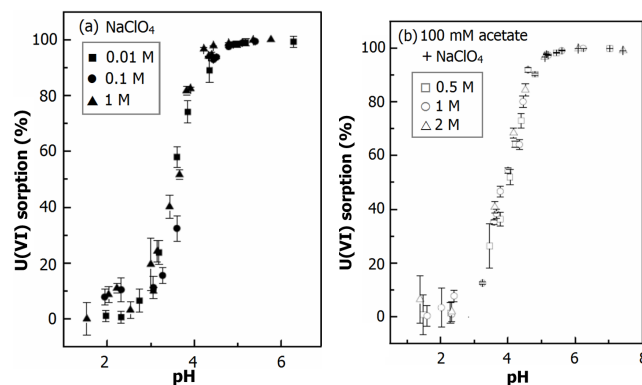
is not needed.

Fig. 3. Sorption of 0.1 mM U(VI) on silica at different $NaClO_4$ concentrations (a), and with 100 mM acetate and 0.5–2 M $NaClO_4$ (b).

The ATR *in-situ* experiments of uranyl sorption on silica layer were performed in 0.1 M NaCl aqueous solutions. The uranyl concentration was chosen at 50 μM to minimize the uranyl signal coming from the aqueous solution (detection limit of the spectroscopy for uranyl soluble species is 0.1 mM). The pH value used was 5.5, so as to have a maximal U(VI) sorption percentage onto silica and avoid the precipitation of U(VI) hydrolyzed species.
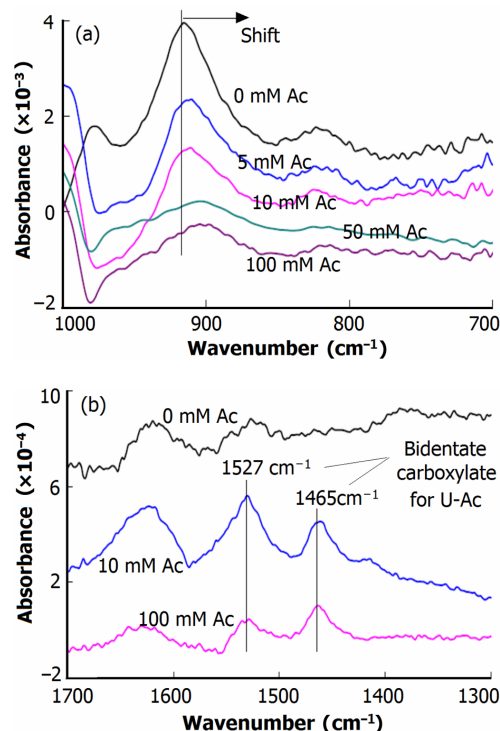

Fig. 4. (Color online) ATR spectra of O=U=O region (a) and carboxylate region (b) for U(VI)-silica, U(VI)-Ac-silica at pH 5.5. The silica film is simultaneously exposed to 50 μM U + 0∼100 mM Ac.

The ATR spectra of ternary systems silica-Ac-U where acetate and uranyl were simultaneously added in aqueous solu-

tion ([U] = 50 μM, [Ac] = 1, 10 and 100 mM) are shown in Fig. 4: $\nu(UO_2)$ in Fig. 4(a) and $\nu(COO)$ in Fig. 4(b). Concerning the O=U=O region, in the absence of acetic acid, the $\nu_a(UO_2)$ band is topped at $916\,cm^{-1}$, which is a shift to lower wavenumber than U(VI) aqueous solution ($928\,cm^{-1}$), obtained under the same conditions (pH and concentrations), indicating a sorption process of inner-sphere type, as already reported in the different papers dealing with the sorption of uranyl ions on oxides [7, 19]. The wavenumber positions are in agreement with the those issued from the literature for uranyl sorbed on silica surface [9].

The increase of acetate concentration from 1 to 100 mM is correlated to intensity decrease of the $\nu_a(UO_2)$ absorption band (Fig. 4(a)), which is in agreement with the macroscopic results (Fig. 1). Moreover, the increase of acetate concentration induces a significant shift of the $\nu_a(UO_2)$ absorption band (from $916\,cm^{-1}$ for binary silica-U to $904\,cm^{-1}$ for ternary silica-U-Ac 100 mM), revealing an evolution of the uranyl surface speciation.

Indeed, the complexation of UO_2^{2+} by "electronegative" ligands weakens the O=U=O bonds, increasing bond lengths and causing shifts to lower frequency of $\nu(UO_2)$, with the extent of this shift related to stability of the uranyl ligand interaction [20]. For example, FT-IR spectra of uranyl ion sorbed on ferric oxides showed an absorption band $\nu(UO_2)$ in the range of $902-925\,cm^{-1}$ with a shift to lower wavenumbers ($888-903\,cm^{-1}$) when surface ternary complexes with carbonate ions were sorbed [21, 22].

The bands at $916\,cm^{-1}$ are not symmetric. This means that more than one sorbed species is present on silica and the deformation of this band might be due to variation of the proportion between the sorbed species caused by addition of the ligands. This result obtained by ATR-FTIR is an essential outcome to understand the role of organic acids in the ternary system: acetic acid not only complexes uranyl ion in aqueous solution, but also participate to the sorption, by forming ternary surface complexes. The curve fitting and decomposition of interested spectra are shown in Fig. 5. In the binary system, the band at $916\,cm^{-1}$ was decomposed (using Gaussian peaks) into 2 bands centered at $918\,cm^{-1}$ and $892\,cm^{-1}$, suggesting two chemical environments of sorbed U(VI) on silica at pH 5.5. The two bands are seen in the ternary system with [Ac] = 10 mM. In the presence of acetic acid, a third band appeared at $904\,cm^{-1}$ for the system of acetate (the dash line). Peaks of the third band were characterized as the sorption of U-carboxylate soluble species on silica. And the third surface species changed effectively relative proportion of the two bands found in the absence of acetate (band at $918\,cm^{-1}$ decreased more evidently than that at $892\,cm^{-1}$). Thus, the presence of acetate would mainly affect the chemical equilibrium formed in binary system. The formation of the ternary surface complex would lead to a subsequent restructuration of binary surface complexes.

To confirm this hypothesis, the spectra of carboxylate bands for silica-U and silica-U-Ac (10 mM and 100 mM) were recorded (Fig. 4(b)). All the ATR spectra (recorded at the same conditions) were subtracted by that of the aqueous acetate at the same concentration: the fingerprint
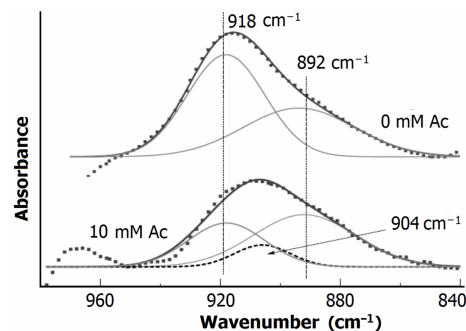

Fig. 5. ATR spectra decomposition of O=U=O region for U(VI)-silica, U(VI)-Ac-silica at pH 5.5.

of U-Ac complexes sorbed onto silica is evidenced by the bands at $1527\,cm^{-1}$ $\nu_a(COO)$ and $1467\,cm^{-1}$ $\nu_s(COO)$. The splitting between the antisymmetric and symmetric stretching ($\Delta\upsilon$) was less than $100\,cm^{-1}$, indicating that the coordination structure between the uranyl ion and the carboxylate group might be "chelating bidentate" [23–25]. It is important to note that with the concentrations of uranyl (50 μM) and acetate (10–100 mM), no fingerprint of aqueous U-Ac complexes was evidenced in the ATR spectra. From the spectrum analysis, it can be concluded that a shift of $\upsilon_3(UO_2^{2+})$ caused by presence of the acids showed the change of uranyl coordination environment at silica-electrolyte interface. The spectrum of sorbed uranyl-acetate complex on silica clearly indicates a bidentate binding of the carboxylate group to the uranyl cation.

B. The adding sequence effect on silica sorption

The sequence effect on silica sorption was studied by adding acetate (100 mM) and uranyl (50 μM) in different orders. Indeed, the addition sequence of a metallic ion and an organic molecule is a parameter to take into account in sorption processes because it has been shown to influence the arrangement of surface complex. Type-A ternary complexes (metal-like) are formed when metallic ion creates a bridge between surface and organics and type-B ternary complexes (ligand-like) correspond to the interaction with the surface through organics. The formation of type-A or type-B complexes sorbed onto mineral surface depends both on the nature of the organic matter and of its concentration: for weak amounts of sorbed organics, type-A complexes are favored [26–28], whereas for greater amounts of sorbed organics, type-B complexes are mainly formed [29, 30]. The sorption of metallic ion can be increased by the preliminary sorption of organics [31] and from zeta potential measurements of Fairhust *et al.* [32] on the retention of Eu(III) in presence of humic acids on boehmite and goethite, the sorption of organics induces a surface charge reversal which induces additional sorption sites for metallic ion retention.

Three sequences of adding sorbents were investigated for the ternary system silica-uranyl-acetate: Sequence 1, acetate sorbed before adding uranyl; Sequence 2, uranyl sorbed be-

TABLE 1. CCM parameters and U(VI) sorption equilibrium determined using FITEQL

Surface reaction	$\log K$ (int)
Surface acidity reaction	
$\equiv \mathrm{Si(OH)_2} \equiv \mathrm{SiO_2H^-} + \mathrm{H^+}$	-7.5
Surface complexation reaction	
$\equiv \mathrm{Si(OH)_2^0} + \mathrm{UO_2^{2+}} \equiv \mathrm{SiO_2UO_2^0} + 2\mathrm{H^+}$	-4.8 ± 0.2
$\equiv \mathrm{Si(OH)_2^0} + \mathrm{UO_2^{2+}} + \mathrm{H_2O} \equiv \mathrm{SiO_2UO_2(OH)^-} + 3\mathrm{H^+}$	-10.2 ± 0.3
$\equiv \mathrm{Si(OH)_2^0} + \mathrm{UO_2^{2+}} + \mathrm{HAc} \equiv \mathrm{SiO_2UO_2Ac^-} + 3\mathrm{H^+}$	-7.4 ± 0.2
Surface parameters	
Site density (sites/nm^2): 0.75	Surface specific area (m^2/g): 380–400
Capacitance (F/m^2): 1.0	

fore adding acetate; and Sequence 3, adding uranyl and acetate simultaneously. The results are illustrated in Fig. 6 for ATR spectra of O=U=O region (Fig. 6(a)), carboxylate region (Fig. 6(b)) and the results of macroscopic measurements (Fig. 6(c)).

It is noted that this experiment was performed by adding the second analyte (U or acetate, and keeping the pH and ionic strength as sorption conditions) after sorption equilibrium of the first analyte adsorption (the continuously recorded FT-IR spectra were stable). Only two sequences were shown in Fig. 6(a) since the addition of $100\,\mathrm{mM}$ acetate decreased the U(VI) absorption band so rapidly and completely that the band intensity was not significant, as it was with $10\,\mathrm{mM}$ acetate. All the spectra show the same pattern for the $\nu_\mathrm{a}(\mathrm{UO_2})$ band in terms of wavenumber position of the sorbed uranyl-acetate species, which traduces no significant effect of the addition order, as observed by batch experiments (Fig. 6(c)). Likewise, all the ATR spectra in the 1200–$1800\,\mathrm{cm^{-1}}$ region (Fig. 6(b)) show the same pattern, such as the presence of the two carboxylate bands at $1527\,\mathrm{cm^{-1}}$ $\nu_\mathrm{a}(\mathrm{COO})$ and $1467\,\mathrm{cm^{-1}}$ $\nu_\mathrm{s}(\mathrm{COO})$ corresponding to the uranyl-acetate complexes sorbed onto silica.

No sequence effect of acetate and uranyl on the sorption on silica in ternary systems U(VI)-acetate-silica was observed from the macroscopic and structural investigations, which induces that the sorption reactions of U-Ac lead to chemical equilibrium. The sorbed systems are in thermodynamical equilibrium whatever the addition order of uranyl and acetate, and the surface speciation is identical. These results are of great importance for modeling the sorption isotherms of this system by surface complexation models.

As no sorption evidence for acetate ion on silica was observed in acetate-silica binary system (macroscopic measurement and spectral analysis), type-A complex for sorbed U(VI)-acetate complex in ternary systems can be concluded.

C. Modeling

Previous EXAFS analysis suggested that the sorbed uranyl ions on silica might form inner sphere mono-silicium bidentate surface complexes [33, 34]. In this study, no outer sphere surface complex was detected. The ionic strength was maintained at $0.1\,\mathrm{M}$ for all sorption systems. Therefore, 2-pK/CCM was used to simulate the complexation reaction of uranyl ion on silica surface. The surface acidity constants (K_1, K_2), site density of silica and the value of Helmholtz capacitance (in the case of CCM) were obtained by fitting potentiometric titration data.

The surface functional groups were defined as the main surface species responsible for the surface complexation. The pH dependent surface charge varies due to the deprotonation reaction according to the following equilibrium:

$$\equiv \mathrm{Si(OH)_2} \equiv \mathrm{SiO_2H^-} + \mathrm{H^+} \qquad K(-), \qquad (2)$$
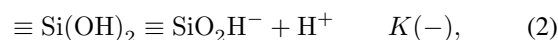
where $K(-)$ is the intrinsic equilibrium constant of the equation. The results of surface acid-base parameters are given in Table 1. The protonation constant $K(+)$ of silica was not considered in the pH range of 2–8 since the value $\log K(+)$ is low (from -2 to 0.5 [35, 36]).

In this study, the relative constants for surface complexation reactions were determined by both macroscopic and structural data, and the information is provided as complete as possible about U(VI) sorption speciation on silica: the dependence of U(VI) sorption on pH and the complexing ligand concentration, the ternary surface complex, the number of sorbed species and their distribution as a function of pH or organic concentration.

The result of U(VI) sorption curve fitting in binary system is shown in Fig. 7(a), and the relative constants $\log \mathrm{K}$ are listed in Table 1. At [uranyl] $= 0.1\,\mathrm{mM}$, [Si(IV)] $< 2\,\mathrm{mM}$ [37], free uranyl ion $\mathrm{UO_2^{2+}}$ and uranyl silicate complex $\mathrm{UO_2H_3SiO_4^+}$ are the dominant soluble species at pH 3. The complex 1 can be attributed to either of the two species sorbed on silica. Meanwhile, the complex 2 can be attributed to the sorption of mono- or polynuclear hydrated species. Several combinations of "complex 1" + "complex 2" were employed to fit the sorption data. An excellent agreement was found for complex 1: $\equiv\mathrm{SiO_2UO_2}$ or $\equiv\mathrm{SiOHUO_2H_3SiO_4}$ and complex 2: $\equiv\mathrm{SiOHUO_2OH^-}$).

The sorption data of the ternary systems were simulated using similar analogy. The fitting results are illustrated in Figs. 7(b) and 7(c). The relative equilibrium constants are summarized in Table 1. Successful fitting of the experimental data was achieved with adding a third surface complex, which was observed by spectroscopic analysis and determined as the sorption of U(VI)-carboxylate soluble species on silica. The complex $\mathrm{UO_2(CH_3COO^-)^+}$ was chosen for the following reasons:
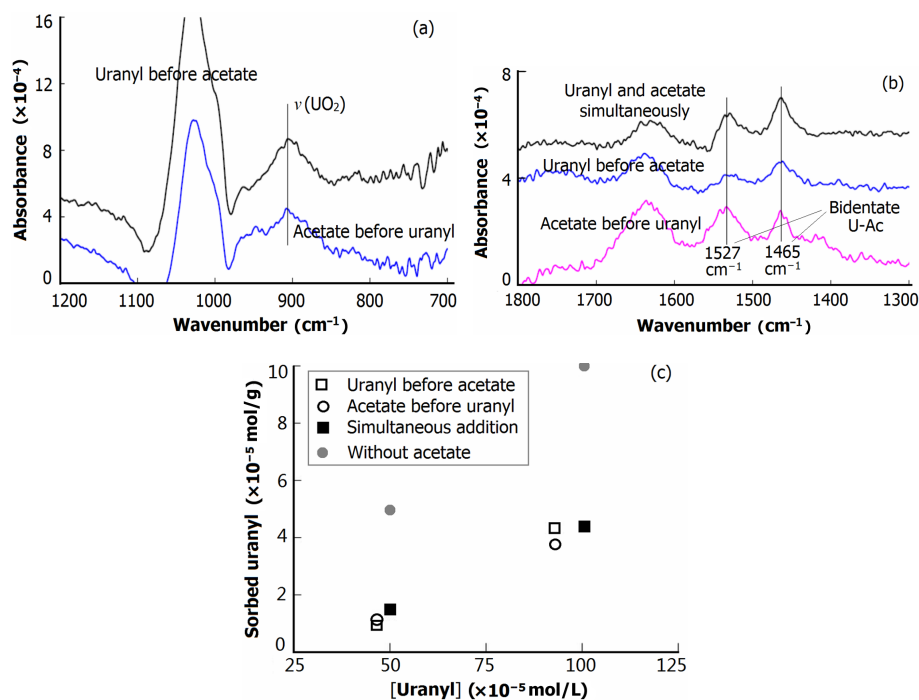
Fig. 6. (Color online) Effect of the order to add 100-mM acetate and 50-μM uranyl on silica sorption at pH 5.5. (a) The ATR spectra of O=U=O region, (b) carboxylate region, (c) macroscopic data for sorption of 0.1 mM U(VI) on silica in absence of acetate (●) and in presence of 0.1 M acetate added in Sequences 1 (□), 2(○) and 3 (■) $\times 10^{-5}$.
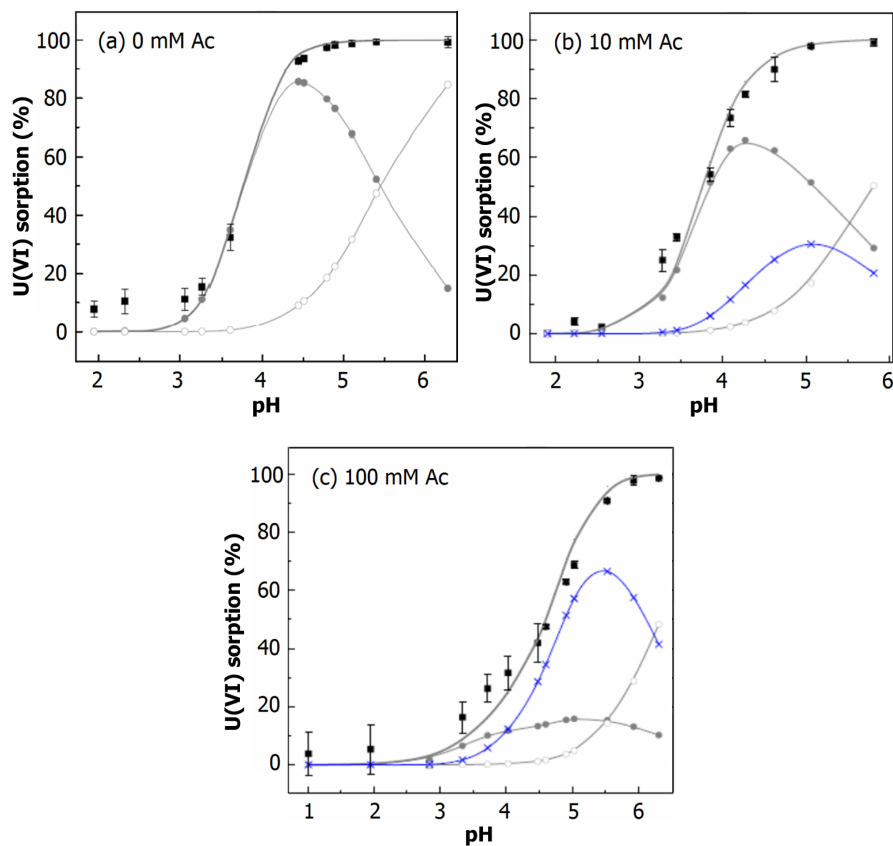

Fig. 7. (Color online) Modeling of U(VI) sorption in absence of Ac (a) and with 10 mM (b) and 100 mM (c) Ac on silica. ●, $\equiv SiO_2UO_2$; ○, $\equiv SiO_2UO_2OH^-$; ×, $\equiv SiO_2UO_2Ac^-$; ■, experimental data.

1) ATR-FTIR spectra showed that the coordination structure between U(VI) and carboxylate group was chelating for the sorbed species, and the site chosen was bidentate. As the coordination number for U(VI) equatorial plane is generally 5–6 [38], it is likely that the sorption of $UO_2(RCOO^-)^+$ on silica is logical.

2) The ternary surface complex appeared from pH = 3 (observed by TRLFS, not shown here), according to the diagram (Fig. 2), $UO_2(RCOO^-)^+$ is predominate at the same pH. The distribution calculated by the model (Figs. 7(b) and 7(c)) confirmed the ATR-FTIR investigations: the increasing contribution of the ternary surface complexes and the decreasing contribution of complex 1 occurred simultaneously when the organics concentration increased. The acetate ion complexed U(VI) in aqueous solution at silica/electrolyte interface.

IV. CONCLUSION

In this paper, two experimental complementary approaches (macroscopic sorption data, and ATR-FTIR for molecular informations both from the carboxylate and from the O=U=O spectral regions) coupled to thermodynamical calculations were successfully applied to study the influence of acetate on the sorption of uranyl ions on silica as well as the addition order in the ternary system silica-U(VI)-acetate. ATR-FTIR result data evidenced for the first time the presence of U-Ac complexes sorbed on silica surface. The two analysis approaches are both complementary and coherent, and evidence that the presence of organic ligand changes U(VI) sorption profile on silica. The acetate ion participates in the uranyl-silica surface complexation.

ATR-FTIR investigations clearly showed the absorption bands characteristic of sorbed U-Ac complexes both from the acetate and uranyl spectral regions, and the coordination structure between U(VI) and carboxylate group was chelating bidentate for the ternary surface complexes. Moreover, no effect of the addition order of acetate and uranyl on the sorption on silica in ternary systems silica-U(VI)-acetate has been evidenced. The sorbed systems are at the thermodynamical equilibrium inducing the possible modeling of all the sorption isotherms of our systems by surface complexation models. The surface reactions with related equilibrium constants were successfully simulated. This study concerning the role of the short-chain carboxylic acids in the uranyl sorption onto silica is of great importance to predict the migration of uranyl ions in the geosphere in the context of the long-term safety of radioactive waste repositories.

[1] Thurman E M. Organic geochemistry of natural waters, Boston (USA): Kluwer Academic Publishers, 1985.

[2] Wei M, Liao J, Liu N, *et al*. Interaction between uranium and humic acid(I): adsorption behaviors of U(VI) in soil humic acids. Nucl Sci Tech, 2007, **18**: 287–293. DOI: 10.1016/S1001-8042(07)60063-3

[3] Ohnuki T and Sasaki T. Effect of pH, ionic strength and humic acid on the sorption of uranium(VI) to attapulgite. J Nucl Sci Technol, 2013, **50**: 863–864. DOI: 10.1016/j.apradiso.2009.03.113

[4] Hug S J. In Situ Fourier Transform Infrared Measurements of Sulfate Adsorption on Hematite in Aqueous Solutions. J Colloid Interf Sci, 1997, **188**: 41–45. DOI: 10.1006/jcis.1996.4755

[5] Lefèvre G. In situ Fourier-transform infrared spectroscopy studies of inorganic ions sorption on metal oxides and hydroxides. Adv Colloid Interfac, 2004, **107**: 107–110. DOI: 10.1006/jcis.1996.4755

[6] Lefèvre G, Noinville S, Fédoroff M. Study of uranyl sorption onto hematite by in situ attenuated total reflection-infrared spectroscopy. J Colloid Interf Sci, 2006, **296**: 608–611. DOI: 10.1016/j.jcis.2005.09.016

[7] Lefèvre G, Kneppers J, Fédoroff M. Sorption of uranyl ion on titanium oxide studied by in situ ATR-FTIR spectroscopy. J Colloid Interf Sci, 2008, **327**: 15–20. DOI: 10.1016/j.jcis.2008.07.044

[8] Müller K, Foerstendorf H. Sorption of U(VI) at the TiO_2–water interface: An in situ vibrational spectroscopic study. Environ Sci Technol, 2009, **43**: 7665–7668. DOI: 10.1016/j.gca.2011.10.004

[9] Müller K. The sorption of uranium(VI) and neptunium (V) onto surfaces of metal oxides and alumosilicates studied by in situ vibrational spectroscopy. Ph.D. Thesis, Institute of Radiochemistry at the Forschungszentrum Dresden-Rössendorf, 2009.

[10] Sladkov V, Zhao Y, Mercier-Bion F. Capillary zone electrophoresis for U(VI) and short chain carboxylic acid sorption studies on silica and rutile. Talanta, 2011, **83**: 1595–1598. DOI: 10.1016/j.talanta.2010.11.055

[11] Schindler P W and Stumm W. Aquatic surface chemistry. NewYork (USA): Wiley, 1987.

[12] Westall J C and Herbelin A L. Report 96-01, chemistry department, Oregon University.

[13] Hayes K F, Papelis C, Leckie J O. Modeling ionic strength effects on anion adsorption at hydrous oxide/solution interface. J Colloid Interf Sci, 1988, **125**: 717–726. DOI: 10.1016/j.talanta.2010.11.055

[14] Grenthe I. Chemical thermodynamics of uranium-NEA OCDE. Wanner H., Forest I., ed., Vol.1, North-Holland, 1992.

[15] Martell A E and Smith R. NIST critical stability constants of metal complexes database. NIST standard reference database 46. Department of commerce. National institute of science and technology. Gaithersburg, Maryland.

[16] Pathak P N and Choppin G R. Kinetics and thermodynamics of uranium (VI) sorption on hydrous silica. Radiochim Acta, 2007, **95**: 245–247. DOI: 10.1524/ract.2007.95.9.507

[17] Bradl H B. Adsorption of heavy metal ions on soils and soils constituents. J Colloid Interf Sci, 2004, **277**: 1–18. DOI: 10.1016/j.jcis.2004.04.005

[18] Hayes K F, Papelis C, Leckie J O. Modeling ionic strength effects on cation adsorption at hydrous oxide/solution interfaces. J Colloid Interf Sci, 1987, **115**: 564–572. DOI: 10.1016/0021-9797(87)90078-6

[19] Sylwester E R, Hudson E A, Allen P G. The structure of uranium(VI) sorption complexes on silica, alumina, and montmorillonite. Geochim Cosmochim Ac, 2000, **64**: 2431–2435. DOI: 10.1016/S0016-7037(00)00376-8

[20] Pasilis S P and Pemberton J E. Pectroscopic investi-

gation of uranyl (VI) and citrate cosorption to Al_2O_3. Geochim Cosmochim Acta, 2008, **72**: 277–281. DOI: 10.1016/j.gca.2007.09.036

[21] Ho C H and Miller N H. Sorption of uranyl species from bicarbonate solution onto hematite particles. J Colloid Interf Sci, 1986, **110**: 165–168. DOI: 10.1016/0021-9797(87)90078-6

[22] Wazne M, Korfiatis G P, Meng X. Carbonate Effects on Hexavalent Uranium Adsorption by Iron Oxyhydroxide. Environ Sci Technol, 2003, **37**: 3619–3624. DOI: 10.1021/es034166m

[23] Mehrotra R C and Bohra R. Metal carboxylates, NewYork (USA): Academic Press, 1983.

[24] Quilès and Burneau A. Infrared and Raman spectroscopic study of uranyl complexes: hydroxide and acetate derivatives in aqueous solution. Vib Spectrosc, 1998, **18**: 61–75. DOI: 10.1016/S0924-2031(98)00040-X

[25] Jiang J, Rao L, di Bernardo P, *et al*. Complexation of uranium(VI) with acetate at variable temperatures. J Chem Soc Dalton, 2002, 1832–1838. DOI: 10.1039/B106642K

[26] Orsetti S. Binding of Pb(II) in the system humic acid/goethite at acidic pH. Chemosphere, 2006, **65**: 2313–2316. DOI: 10.1016/j.chemosphere.2006.05.009

[27] Ali M A and Dzombak D A. Geochim Cosmochim Acta, 1996, **60**: 291–294. DOI: 10.1016/0016-7037(95)00385-1

[28] Song Y, Swedlund P J, Singhal N. Copper(II) and cadmium(II) sorption onto Ferrihydrite in the presence of phthalic acid: some properties of the ternary complex. Environ Sci Technol, 2008, **42**: 4008–4011. DOI: 10.1021/es702509q

[29] Lee S S, Nagy K L, Fenter P. Distribution of barium and fulvic acid at the mica–solution interface using in-situ X-ray reflectivity. Geochim Cosmochim Acta, 2007, **71**: 5763–5766. DOI: 10.1016/j.gca.2007.05.031

[30] Alcacio T E. Molecular scale characteristics of Cu(II) bonding in goethite–humate complexes. Geochim Cosmochim Acta, 2001, **65**: 1355–1359. DOI: 10.1016/S0016-7037(01)00546-4

[31] Tipping E, Griffith J, Hilton J. A unifying model of cation binding by humic substances. Croat Chem Acta, 1983, **56**: 613–617. DOI: 10.1016/0016-7037(92)90158-F

[32] Fairhurst A J and Warwick P. The influence of humic acid on europium–mineral interactions. Colloid Surf A, 1998, **145**: 229–233. DOI: 10.1016/S0927-7757(98)00662-1

[33] Reich T. An EXAFS study of uranium(VI) sorption onto silica gel and ferrihydrite. J Electron Spectrosc, 1998, **96**: 237–243. DOI: 10.1016/S0368-2048(98)00242-4

[34] Sylwester E R, Hudson E A, Allen P G. The structure of uranium(VI) sorption complexes on silica, alumina, and montmorillonite. Geochim Cosmochim Ac, 2000, **64**: 2431–2438. DOI: 10.1016/S0016-7037(01)00546-4

[35] Oelkers E H. The surface chemistry of multi-oxide silicates. Cosmochim Acta, 2009, **73**: 4617–4634. DOI: 10.1016/j.gca.2009.05.028

[36] Stamberg K, Venkatesan K A, Vasudeva Rao P R. Surface complexation modeling of uranyl ion sorption on mesoporous silica. Colloid Surf A, 2003, **221**: 149–162. DOI: 10.1016/S0927-7757(03)00139-0

[37] Soderholm L and Skanthakumar S. Characterizing solution and solid-phase amorphous uranyl silicates. Geochim Cosmochim Acta, 2008, **72**: 140–150. DOI: 10.1016/j.gca.2007.10.002

[38] Choppin G R. Solution chemistry of the actinides. Radiochim Acta, 1983, **32**: 43–53. DOI: 10.1524/ract.1983.32.13.43